

## A Revised Disrupted Langmuir-Adsorption Model of Photocatalysis

Mills, A., & O'Rourke, C. (2015). A Revised Disrupted Langmuir-Adsorption Model of Photocatalysis. *Journal of Physical Chemistry C*, 119(34), 19941-19946. <https://doi.org/10.1021/acs.jpcc.5b05787>

**Published in:**  
Journal of Physical Chemistry C

**Document Version:**  
Peer reviewed version

**Queen's University Belfast - Research Portal:**  
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Journal:	<i>The Journal of Physical Chemistry</i>
Manuscript ID:	jp-2015-057877
Manuscript Type:	Article
Date Submitted by the Author:	17-Jun-2015
Complete List of Authors:	Mills, Andrew; Queen's University Belfast, School of Chemistry and Chemical Engineering O'Rourke, Christopher; Queen's University Belfast, School of Chemistry and Chemical Engineering

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A revised disrupted Langmuir-adsorption model of photocatalysis

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**Keywords:** Photocatalysis, Titania, Mechanisms, Kinetics, Models.

## Abstract

The increasingly popular disrupted Langmuir-adsorption kinetic model of photocatalysis does not containing an explicit function for the dependence of rate on the irradiance,  $\rho$ , but instead has a term  $\alpha\rho^\theta$ , where,  $\alpha$  is a constant of the system, and  $\theta$  is also a constant equal to 1 or 0.5 at low or high  $\rho$  values, respectively. Several groups have recently replaced the latter term with an explicit function of the form  $\chi_1(-1 + (1 + \chi_2\rho)^{1/2})$ , where  $\chi_1$  and  $\chi_2$ , are constants that can be related to a proposed reaction scheme. Here the latter schemes are investigated, and revised to create a more credible form by assuming an additional hole trapping step. The latter may be the oxidation of water or a surface saturated with  $\text{O}_2^-$ . Importantly, this revision suggests that it is only applicable for low quantum yield/efficiency processes. The revised disrupted Langmuir-adsorption model is used to provide good fits to the kinetic data reported for a number of different systems including the photocatalytic oxidation of: nitric oxide (NO), phenol (PhOH) and formic acid (FA).

## Background

The commonly observed kinetics of photocatalysis, in liquid and gas phase, has often been reported<sup>1,2</sup> as having the following form:

$$r_i = \alpha \rho^\theta \{K^*_L[P]_b / (1 + K^*_L[P]_b)\} = k(max)\{K^*_L[P]_b / (1 + K^*_L[P]_b)\} \quad (1)$$

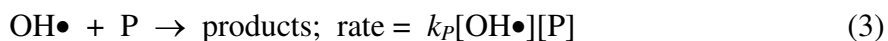
where  $r_i$  is the initial rate,  $\rho$  is the incident irradiance,  $\alpha$  and  $k(max)$  ( $= \alpha \rho^\theta$ ) are proportionality constants, which vary from test system to test system and P is the test pollutant and  $[P]_b$  is its bulk concentration. The power term,  $\theta$ , has values of 1 and 0.5 at low and high  $\rho$  values, respectively, and  $K^*_L$  is the apparent Langmuir adsorption constant, derived from measurements of the photocatalysed initial rate as a function of  $[P]_b$ . Not surprisingly, this type of kinetics is often referred<sup>1,2</sup> to as Langmuir- or Langmuir-Hinshelwood-type kinetics and one of the most-quoted, seminal works on the observed kinetics of photocatalysis, that of Ollis and Turchi published in 1990<sup>2</sup>, describe four scenarios, which were eminently reasonable at the time, in which the above commonly observed kinetics for photocatalysis, as described by eqn(1), were derived, based on OH• radical attack on P. The four scenarios considered were where: (I) both species (P and OH•) adsorbed, (II) P adsorbed, OH• non-bound, (III) P non-bound, OH• adsorbed and (IV) both P and OH• non-bound.

It is now accepted that in most cases of photocatalysis, which exhibit kinetics that ostensibly fit eqn (1),  $K^*_L$  is itself a function of  $\rho$ , and as a result the simple Langmuir type rate expression, of the form of eqn (1), is no longer appropriate in such cases<sup>3</sup>. As part of many efforts to address this revised appreciation of the general form of the kinetics of photocatalysis, in 2005 Ollis

proposed<sup>5</sup> an alternative, attractive, simple kinetic model, based on the non-equilibrated (often referred to as 'disrupted')<sup>4</sup> adsorption of P, in which it was shown that the initial rate is given by:

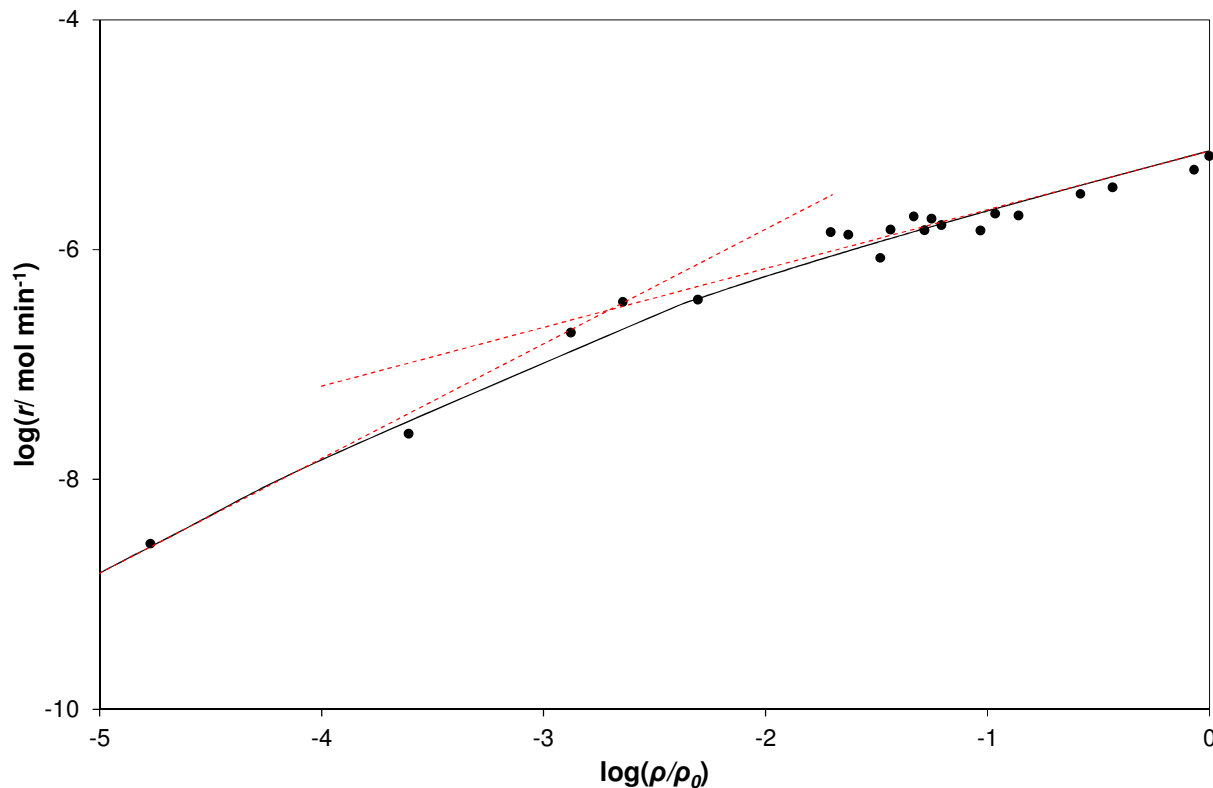
$$r_i = \chi_1 \rho^\theta [P]_b / (1 + \chi_2 \rho^\theta + \chi_3 [P]_b) \quad (2)$$

where:  $\chi_1 = \alpha K_L [S]_0$ ;  $\theta = \text{constant}$ , such that  $0.5 \leq \theta \leq 1$ , and  $\chi_2 = \alpha/k_{des}$ ;  $\chi_3 = K_L$ , and  $\alpha$  is a proportionality,  $K_L$  is the Langmuir adsorption constant (Units:  $M^{-1}$ ),  $[S]_0$  is the concentration of adsorption sites on the semiconductor (units: M) and  $k_{des}$  is the rate constant for the desorption of P, the pollutant, from the semiconductor's surface (units:  $s^{-1}$ ). A key feature of this, increasingly employed<sup>6-10</sup>, disrupted Langmuir adsorption kinetic model is the reaction between P and a trapped hole. Ollis<sup>5</sup> and others<sup>7,9,10</sup> suggest that the trapped hole is in the form of an hydroxyl radical,  $OH^\bullet$ , via a reaction with surface adsorbed water or  $OH^-$  groups. Others<sup>11-13</sup> have suggested that such a reaction is not possible and, instead, the trapped hole arises from reaction with terminal oxygen ions,  $>O_s^{2-}$ . In this work, just in terms of the rate equations, it doesn't matter which of these forms the trapped hole takes, but, for simplicity and consistency with the original mechanism proposed by Ollis<sup>5</sup> and adopted by others<sup>6-10</sup>, we shall focus on the popular view of hole trapping with the generation of a  $OH^\bullet$  radical. In the Ollis disrupted adsorption model<sup>5</sup> the removal of P occurs via the following reaction:



and it is assumed that the steady-state concentration of  $OH^\bullet$ , and thus the rate, is proportional to  $\rho^\theta$ , where  $\theta$  can lie in the range  $0.5 \leq \theta \leq 1$ , but is 0.5 at high  $\rho$  and 1 at low  $\rho$ ; note:  $[OH^\bullet]$  and  $[P]$  are the surface concentrations of  $OH^\bullet$  and P, respectively.

A brief inspection of both eqns(1) and (2) shows that the assumption that rate is proportional to  $\rho^\theta$  is made in both kinetic models and a current criticism<sup>12,13</sup> of the now largely discredited simple Langmuir kinetics as described by eqn (1), and the increasingly popular disrupted Ollis Langmuir adsorption kinetics, as described by eqn (2), is that they both lack an explicit function for  $\rho$  in the latter rate expressions. Thus, instead of the term ' $\alpha\rho^\theta$ ', which functions to describe the rate constant for the photocatalytic oxidation of P at either low or high  $\rho$  values, what is a required is a credible function that allows  $\rho$  to change smoothly its order from 1 to 0.5 as the irradiance is increased from low to high values. A striking practical example of the latter feature is to be found in the reported<sup>14</sup> variation in initial rate of oxidation of *iso*-propanol (IPA), by dissolved oxygen, photocatalysed by rutile TiO<sub>2</sub>, as illustrated in figure 1. From these results, it is clear that whilst the variation in rate in the extreme regions of  $\rho$  are adequately described by the term ' $\rho^\theta$ ', this is not the case for the transition zone, where the rate is neither proportional to  $\rho$  or  $\rho^{0.5}$ .



**Figure 1.** Plot of  $\log(r_i)$  vs the relative photon flux,  $(\rho/\rho_o)$ , where  $\rho_o = 2.06 \times 10^{18}$  photons  $s^{-1}$ , reported by Egerton and King<sup>14</sup> in their study of the photocatalysed oxidation of IPA by dissolved  $O_2$ , using rutile  $TiO_2$ . The solid line is the line of best fit to the data, calculated using a simplified version of the revised Ollis disrupted adsorption model, eqn (13), and optimised fit values for  $\chi_1[P]_b$  and  $\chi_2 = 1.78 \times 10^{-7}$  mol  $min^{-1}$  and 1730 respectively.

It would not be appropriate to provide here a detailed proof of the kinetic expression for the disrupted Langmuir-adsorption model of photocatalysis, when it is very well described elsewhere<sup>5</sup> but, briefly, it is assumed a steady state concentration in the fraction of occupied adsorption sites,  $f$ , ( $= [P]/[S]_o$ ) is set up, so that:

$$f(k_{des} + \alpha \rho^\theta) = k_{ads}[P]_b(1-f) \quad (4)$$



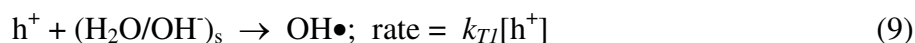
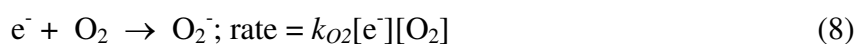
and, thus,

$$[P] = K_L[P]_b[S]_o / (1 + \alpha\rho^\theta/k_{des} + K_L[P]_b) \quad (5)$$

Which then allows the rate expression eqn(2) to be derived, given rate =  $\alpha\rho^\theta[P]$ .

### A quadratic dependence upon irradiance

In order to address this apparent deficiency, several authors<sup>7,9</sup> have used a simple reaction sequence that appears to provide the necessary explicit function, without affecting the other parts of the proposed kinetic scheme, i.e.



where  $h^+$  and  $e^-$  are free photogenerated surface holes and electrons, respectively,  $(\text{H}_2\text{O}/\text{OH}^-)_s$  are surface-adsorbed water/hydroxyl groups and all concentrations refer to surface concentrations. Assuming, under constant illumination, steady-state concentrations in  $[h^+]$  and  $[e^-]$  are generated, it follows that:

$$d[h^+]/dt = 0 = k_0\rho - k_r[h^+][e^-] - k_{TI}[h^+] \quad (10)$$

$$d[e^-]/dt = 0 = k_0\rho - k_r[h^+][e^-] - k_{O2}[e^-][\text{O}_2] \quad (11)$$

Thus,

$$(k_r/k_{O_2}[O_2])[h^+]^2 + [h^+] - k_0\rho/k_{TI} = 0 \quad (12)$$

which, upon solving the *quadratic*, yields the following expression for the steady state concentration of  $h^+$ :

$$[h^+]_{ss} = (k_{O_2}[O_2]/2k_r)(-1 + (1 + 4k_r k_0 \rho / (k_{TI} k_{O_2} [O_2]))^{1/2}) \quad (13)$$

The above quadratic (solution) expression in  $\rho$  (but, note, NOT in  $[P]$ ) appears to provide the desired explicit function for  $\rho$  which can be used in the overall rate expression that allows  $\rho$  to change its order from 1 to 0.5 as the irradiance is increased from low to high values.

### Disconnected kinetic schemes and rate expressions

How researchers have used eqn(13) in order to derive an expression for the overall rate is varied. For example, some<sup>7-9</sup> have assumed reaction (3) is the key process for the removal of P, so that  $d[P]/dt = -k_P[OH\bullet]_{ss}[P]$ , and that  $[OH\bullet]_{ss}$  proportional to  $[h^+]_{ss}$ , which it is, since, from reactions (3) and (9), it follows that under steady-state conditions:

$$k_{TI}[h^+] = k_P[OH\bullet][P] \quad (14)$$

i.e.  $[OH\bullet]_{ss} = k_{TI}[h^+]_{ss}/k_P[P]$ . For example, both Imoberdorf et al.<sup>8</sup>, in their study of the photocatalysed oxidation of tetrachloroethylene, and Yu et al.<sup>7</sup>, in a study the photocatalysed oxidation of NO, use an expression that has  $[OH\bullet]_{ss}$  proportional to the ratio  $[h^+]_{ss}/[P]$ . But, a quick inspection of these expressions and eqn(14) reveals an impossibility, namely, if  $[P] = 0$ ,

[OH•]<sub>ss</sub> = ∞, since, as noted previously, in eqn(13) [h<sup>+</sup>]<sub>ss</sub> is independent of [P]. Thus, it would appear, in such examples<sup>7-9</sup> where it is assumed that the only fate of the free holes is to react with P, the use of eqn(13) to provide an explicit dependence of rate upon ρ, as derived using the simple processes (3), (6)-(9), the assumption is flawed.

Fortunately, this concern is easily resolved via the addition of a simple trapping step, namely:



where T is a hole trap and T<sup>+</sup> is its oxidised form that does not interfere with the reaction, i.e. it is an irreversible oxidation step. Such a process has been proposed previously in another popular mechanism<sup>15</sup>, and so is not without precedent. This additional step may be the oxidation of water or that of a surface saturated with O<sub>2</sub><sup>-</sup>, generated via reaction (8).

If this additional step is adopted, then eqn(14) becomes:

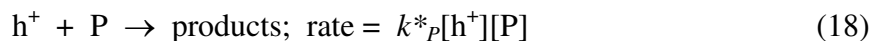
$$[\text{OH}\bullet]_{\text{ss}} = k_{T1}[\text{h}^+]_{\text{ss}}/(k_P[\text{P}] + k_{T2}) \quad (16)$$

Where [h<sup>+</sup>]<sub>ss</sub> is given by eqn (13), i.e. the rate of removal of P would be given by

$$d[\text{P}]/dt = -[\text{P}]\chi_1(-1 + (1 + \chi_2\rho)^{1/2}) \quad (17)$$

but with  $\chi_1 = k_{T1}k_Pk_{O2}[\text{O}_2]/(2k_r(k_P[\text{P}] + k_{T2}))$  and  $\chi_2 = 4k_rk_0/(k_{T1}k_{O2}[\text{O}_2])$ . If it is further assumed that  $k_{T2} \gg k_P[\text{P}]$ , i.e. that it is a low quantum yield process, then  $\chi_1 = k_{T1}k_Pk_{O2}[\text{O}_2]/(2k_rk_{T2})$  and the rate expression has same form as eqn(17), with the desired quadratic dependence of rate upon ρ, but NOT [P].

Alternatively, others<sup>6</sup> have assumed the key oxidation process is direct hole oxidation of P, i.e.



so that the rate of reaction, i.e.  $d[P]/dt = -k_p^*[h^+]_{ss}[P]$ , is related directly to the quadratic expression eqn (13) involving just  $\rho$ . But, in making this assumption it appears an important ramification has been overlooked, namely, that if this were the case then the rate expression in eqn (16) would need to be added to eqn(10), thereby altering the original steady-state expression for  $[h^+]_{ss}$ , eqn (13), and this apparent oversight creates a disconnection between the proposed kinetic scheme and the final rate expression.

This disconnection doesn't have to exist, if the explicit assumption is made that  $k_p[h^+][P]$  is both  $\ll k_r[h^+][e^-]$  and  $\ll k_{TI}[h^+]$ , i.e. that the oxidation of P is a minor process, compared to the other two  $h^+$  decay processes. However, in making the latter assumption, and allowing the use of eqn(13) as an expression of  $[h^+]_{ss}$  to be used in the rate expression for reaction (18), it follows that the quantum yield/quantum efficiency for the process must be necessarily low, unless a radical chain reaction mechanism pertains<sup>16</sup>; since in the latter case quantum yields/efficiencies  $> 1$  can be achieved. Assuming the actual oxidation of P is a minor decay process for  $h^+$ , then the rate of reaction would be given by eqn(17) with,  $\chi_1 = k_p^*k_{O_2}[O_2]/2k_r$  and  $\chi_2 = 4k_r k_0/(k_{TI}k_{O_2}[O_2])$ . Eqn(17) is the form commonly used by groups to describe the rate of removal of P, when using the Langmuir model, eqn (1)<sup>10</sup>, or the disrupted adsorption model, eqn (2)<sup>6-9</sup>, but with the term: ' $\alpha\rho^{\theta}$ ' replaced by the quadratic expression in  $\rho$  (i.e.  $\chi_1(-1 + (1 + \chi_2\rho)^{1/2})$ ). Note: the trapping step, reaction (9) used here produces an  $OH\bullet$  radical, which appears inappropriate if one of its necessary features is that the product has little or no influence on the overall rate expression. Instead, it would appear more reasonable to replace reaction (9) with an alternative trapping step:



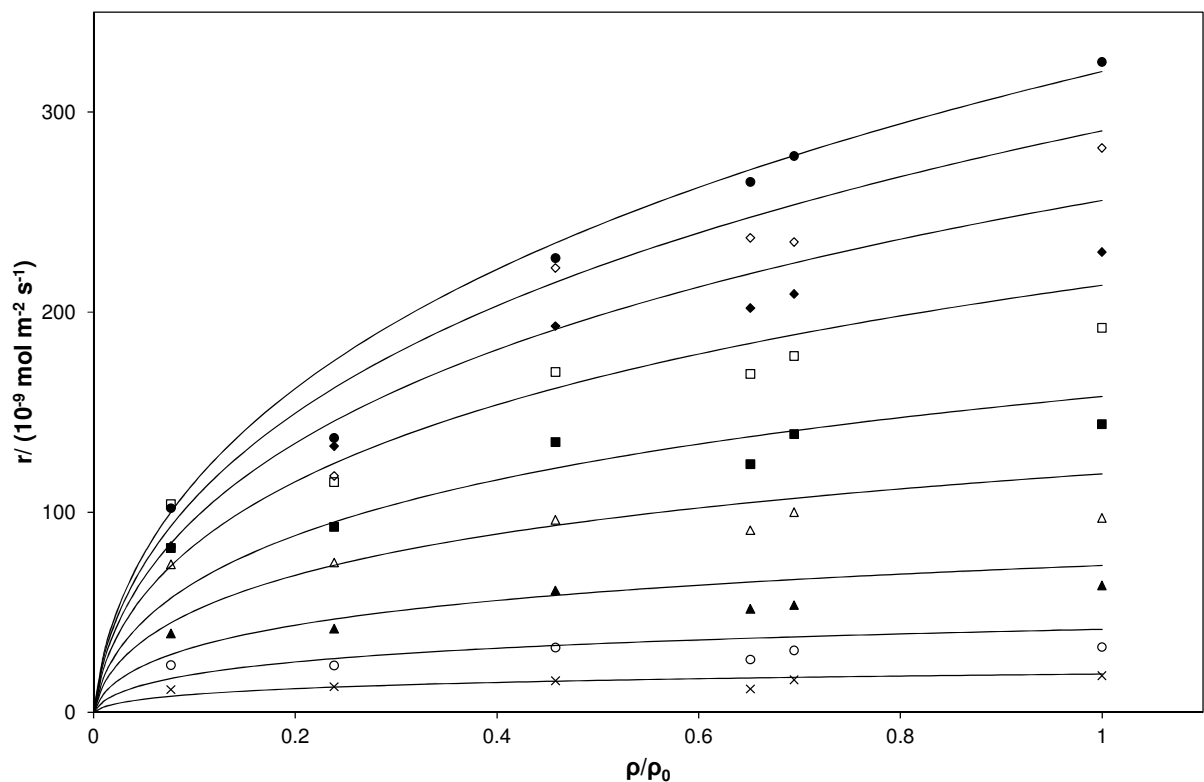
where T is a hole trap such that  $T^+$  does not subsequently directly influence the kinetics of the oxidation process, i.e. it is an irreversible oxidation step. As before, this additional step may, for example, be the oxidation of water or that of a photocatalyst surface saturated with  $O_2^-$ , generated via reaction (6). Under such circumstance,  $\chi_1 = k^*pk_{O_2}[O_2]/2k_r$  and  $\chi_2 = 4k_r k_d/(k_{T_2}k_{O_2}[O_2])$  in the term ' $\chi_1(-1 + (1 + \chi_2\rho)^{1/2})$ ' which replaces the term ' $\alpha\rho^\theta$ ' in eqns (1) and (2).

Earlier it was noted that Egerton and King<sup>14</sup> had reported the observed variation in rate of the photocatalysed oxidation of IPA as a function of  $\rho$  over a sufficiently large range ((0.025 – 103) $\times 10^{16}$  photons  $m^2 s^{-1}$ ) so as to show clearly the rate as being proportional and then half-order at low and high  $\rho$  values, respectively. These two different dependencies are identified here in the plot of the original data in figure 1, by the two red lines. The solid black line, however, is a plot of the line of best fit to the data using the rate, as expressed by eqn(17), and fitting constants  $\chi_1[P]_b$  and  $\chi_2 = 1.78 \times 10^{-7}$  mol  $min^{-1}$  and 1730 respectively. The above provides one example of the apparent appropriateness of the  $\chi_1(-1 + (1 + \chi_2\rho)^{1/2})$  expression derived above as an explicit function that describes the effect of incident irradiation on the initial rate of photocatalysis for most reactions. This function embraces the usually observed linear dependence at low  $\rho$  values and square-root dependence at high  $\rho$ , and provides a smooth transition between the two zones.

Further support for this function can be found from the work of others<sup>6-10</sup>. For example, several research groups<sup>6-9</sup> have revised the Ollis disrupted Langmuir adsorption model, assuming P is oxidised by  $OH^\bullet$ , via reaction (3), by substituting the ' $\alpha\rho^\theta$ ' term for  $\chi_1(-1 + (1 + \chi_2\rho)^{1/2})$  so that

$$r_i = \frac{[P]_b \chi_1 \left( -1 + (1 + \chi_2 \rho)^{1/2} \right)}{1 + \chi_3 \left( -1 + (1 + \chi_2 \rho)^{1/2} \right) + \chi_4 [P]_b} \quad (20)$$

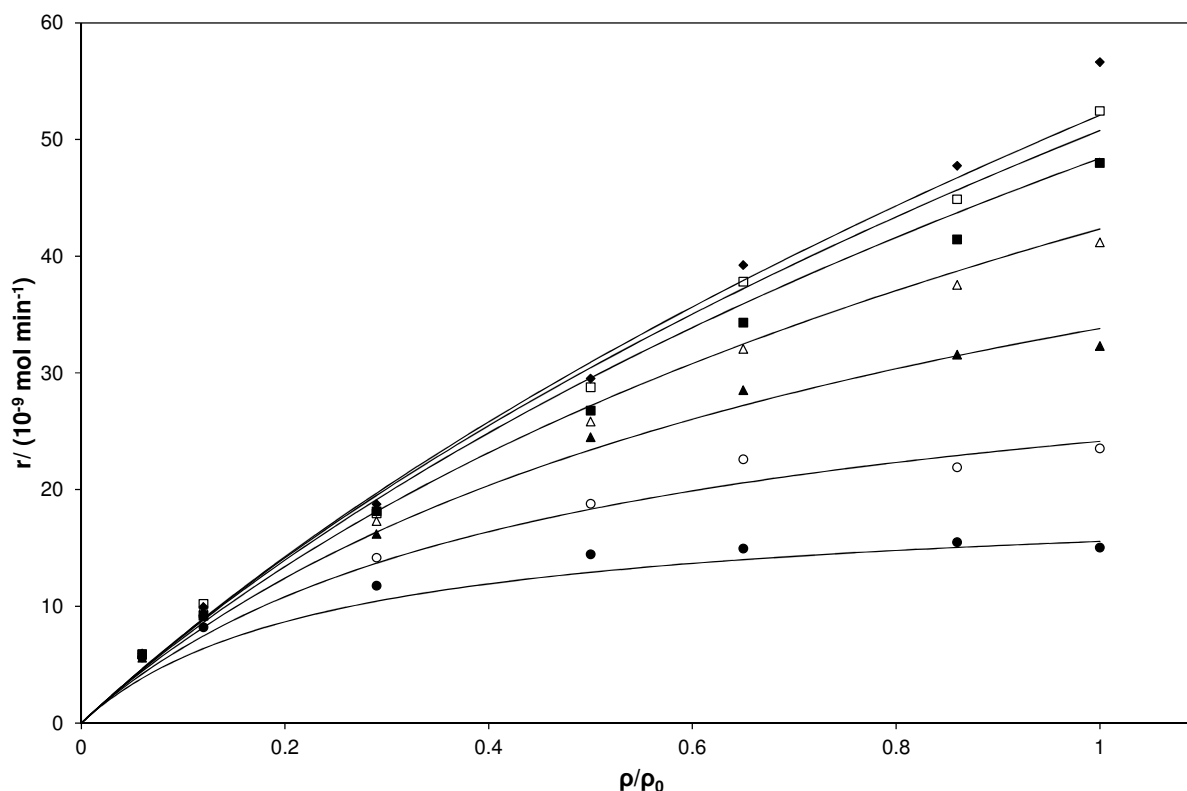
where,  $\chi_1 = k_p k_{T1} (k_{O2} [O_2] / (2k_r k_{T2})) K_L [S]_0$ ;  $\chi_2 = 4k_r k_{O1} / (k_{T1} k_{O2} [O_2])$ ;  $\chi_3 = k_p k_{T1} (k_{O2} [O_2] / (2k_r k_{T2})) / k_{des}$ ;  $\chi_4 = K_L$ . To date, this revised model has been used primarily to fit the observed variation in initial rate for the photocatalysed oxidation of  $NO^{6,7}$ , sensitised by P25  $TiO_2$ , as a function of both  $\rho$  and  $[P]$ , for example by Dillert et al.<sup>6</sup>, as illustrated in figure 2.



**Figure 2.** Plot of  $\log(r_i)$  vs the relative photon flux,  $(\rho/\rho_o)$ , where  $\rho_o = 44.8 \times 10^{-6}$  mol photons  $\text{m}^{-2} \text{s}^{-1}$ , reported by Dillert et al.<sup>6</sup> in their study of the photocatalysed oxidation of NO by  $\text{O}_2$ , using a P25  $\text{TiO}_2$  film. Each solid line is the line of best fit to the data, calculated using the revised Ollis disrupted adsorption model, eqn (18), and optimised fit values for  $\chi_1$ ,  $\chi_2$ ,  $\chi_3$  and  $\chi_4 =: 1.56 \times 10^{-3} \text{ m s}^{-1}$ , 450, 0.0638 and  $4.87 \times 10^4 \text{ m}^3 \cdot \text{mol}^{-1}$ , respectively. The lines correspond to the following [NO] values: [NO] = (●)  $4.58 \times 10^{-5}$ , (◇)  $3.81 \times 10^{-5}$ , (◆)  $3.06 \times 10^{-5}$ , (□)  $2.30 \times 10^{-5}$ , (■)  $1.51 \times 10^{-5}$ , (△)  $1.06 \times 10^{-5}$ , (▲)  $5.99 \times 10^{-6}$ , (○)  $3.21 \times 10^{-6}$ , and (×)  $1.43 \times 10^{-6} \text{ mol m}^{-3}$ .

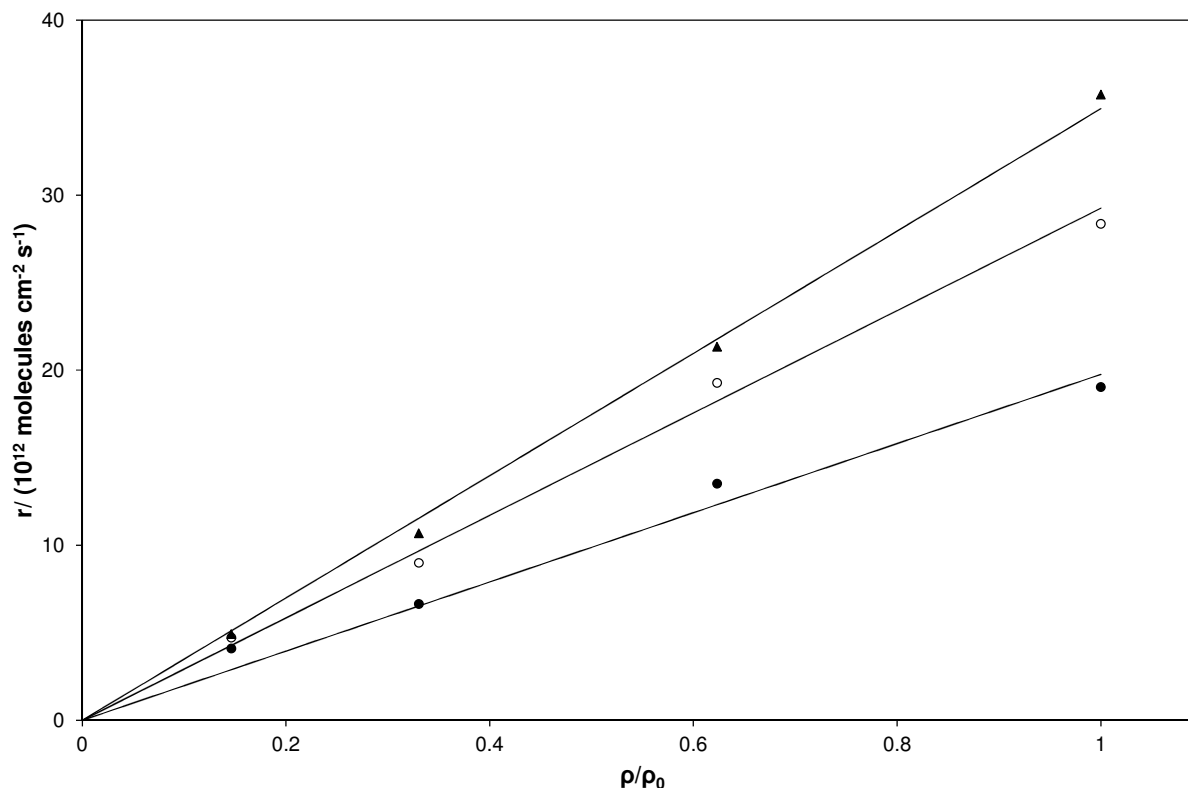
However, it can also be used to fit with equal success, the kinetic results arising from other, similar, probing photocatalytic studies, such as that of oxidation of phenol ( $\text{PhOH}$ )<sup>15</sup>, see

figure 3, reported by Emeline et al., and of formic acid (FA), see figure 4, as reported by Montoya et al.<sup>13</sup>.



**Figure 3.** Plot of  $\log(r_i)$  vs the relative photon flux,  $(\rho/\rho_0)$ , where  $\rho_0 = 1.1 \times 10^{17} \text{ photons cm}^{-2} \text{ s}^{-1}$ , reported by Emeline et al.<sup>15</sup> in their study of the photocatalysed oxidation of PhOH by dissolved  $\text{O}_2$ , using P25  $\text{TiO}_2$ . Each solid line is the line of best fit to the data, calculated using the revised Ollis disrupted adsorption model, eqn (18), in which it is assumed  $\chi_3(-1 + (1 + \chi_2\rho)^{1/2}) \gg 1$  and optimised fit values for  $\chi_1$ ,  $\chi_2$ ,  $\chi_3$  and  $\chi_4$  =:  $9.02 \times 10^{-4} \text{ mol min}^{-1} \text{ M}^{-1}$ , 2.50, 1.13 and  $1.39 \times 10^4 \text{ M}^{-1}$ , respectively. The lines correspond to the following  $[\text{PhOH}]$  values:  $[\text{PhOH}]$  =: ( $\blacklozenge$ ) 0.851, ( $\square$ ) 0.638, ( $\blacksquare$ ) 0.427, ( $\triangle$ ) 0.213, ( $\blacktriangle$ ) 0.106, ( $\circ$ ) 0.053, and ( $\bullet$ ) 0.027 mM.





**Figure 4.** Plot of  $\log(r_i)$  vs the relative photon flux,  $(\rho/\rho_o)$ , where  $\rho_o = 6.2 \times 10^{15} \text{ photons cm}^{-2} \text{ s}^{-1}$ , reported by Montoya et al.<sup>13</sup> in their study of the photocatalysed oxidation of FA by dissolved  $\text{O}_2$ , using P25  $\text{TiO}_2$ . Each solid line is the line of best fit to the data, calculated using a simplified version of the revised Ollis disrupted adsorption model, eqn (18), in which it is assumed  $\chi_3 = 0$  and optimised fit values for  $\chi_1$ ,  $\chi_2$  and  $\chi_4 = 8.93 \times 10^{18} \text{ molecules cm}^{-2} \text{ s}^{-1} \text{ M}^{-1}$ , 0.0415 and  $4280 \text{ M}^{-1}$ , respectively. The lines correspond to the following  $[\text{PhOH}]$  values:  $[\text{PhOH}] = (\blacktriangle) 1.02$ ,  $(\circ) 0.50$ , and  $(\bullet) 0.199 \text{ mM}$ .

Note, that in the latter case, the best fit to the data was obtained with the  $\chi_3 = 0$  and, under such circumstances, the overall rate equation, eqn(20), transforms into that associated with simple Langmuir adsorption kinetics, i.e. eqn (1), but with  $\alpha\rho^\theta = \chi_1(-1 + (1 + \chi_2\rho)^{1/2})$ , i.e.

$$r_i = \frac{[P]_b \chi_1 (-1 + (1 + \chi_2 \rho)^{1/2})}{1 + \chi_3 [P]_b} \quad (21)$$

where,  $\chi_1 = k_p k_{TI} (k_{O_2} [O_2] / (2k_r k_{T2})) K_L [S]_0$ ,  $\chi_2 = 4k_r k_0 / (k_{TI} k_{O_2} [O_2])$  and  $\chi_3 = K_L$ . This suggests that the simple Langmuir rate expression, so often used previously in photocatalysis and now considered redundant<sup>3</sup>, may still have a role to play when rationalising the observed kinetics of some photocatalytic systems, such as the photocatalysed oxidation of FA described above, and illustrated in figure 4, in which there is strong (chemisorption) binding between P and the semiconductor. Evidence for the latter, in the FA/Aldrich TiO<sub>2</sub> system studied by Montoya et al.<sup>13</sup>, is provided by the high (5370 M<sup>-1</sup>) value of  $K_L$ , as measured via a dark adsorption study<sup>13</sup>, which compares well with that ( $\chi_3 = K_L = 4280 \text{ M}^{-1}$ ) extracted here from the best fit of the data (see figure 4) to the revised Langmuir kinetics eqn (21).

It is worth mentioning briefly at this point there is an alternative collection of photocatalysis kinetic models, which are referred to here as 'quadratic 'P' type' kinetic models, in that they predict a quadratic dependence upon  $[P]^{-1}$ , as well as upon  $\rho$ . Quadratic 'P' type kinetic models are very different to the more traditional Langmuir type kinetic models, such as represented by eqns (1) and (2), and their revised forms, namely, eqns(20) and (21), respectively.

As an illustration, the simplest example of such a model is that proposed by Gerischer<sup>17</sup> in 1995, and later used by Upadhy and Ollis<sup>18</sup> in their interpretation of the observed kinetics of the photocatalysed oxidation of trichloroethylene, TCE. In the Gerischer model<sup>17</sup>, reactions (6)-(8) are combined with the direct oxidation of P, i.e. reaction (18), to yield the following expression for the overall rate:

$$d[P]_Q/dt = -[P] \chi_1 (-1 + (1 + \chi_2 \rho)^{1/2}) \quad (22)$$

where,  $\chi_1 = k^*_p k_{O_2}[O_2]/2k_r$  and  $\chi_2 = 4k_r k_0/(k^*_p[P]k_{O_2}[O_2])$ ; a subscript 'Q' has been added to distinguish it from the previously discussed kinetic models, and the rate expression eqn (17), in which, in contrast to eqn(22), the quadratic dependence on rate extended to  $\rho$ , but NOT [P]. Equation (22) is the basic form of the various reported quadratic 'P' type kinetic expressions, derived using subtly different kinetic schemes, such as those proposed by Gerischer<sup>17</sup>, Minero et al.<sup>19,20</sup> and Salvador et al.<sup>12,13</sup>. In all cases, it follows that at high [P] and low [P] values the rate is expected to be zero or half order with respect to [P], since  $\chi_2$  is proportional to  $([P][O_2])^{-1}$ . Unfortunately, in practice, for most reported examples of photocatalysis<sup>1,2</sup>, at low [P] the rate is found to be proportional to [P], and not  $[P]^{0.5}$ . In contrast, Langmuir-type kinetics, as described by rate expressions (1) and (2), and eqns(20) and (21), predict the commonly found independent and proportional dependence of rate upon [P] at high and low values, respectively. As a consequence, quadratic 'P' type kinetic models have found less support than those based on Langmuir type kinetics, i.e. eqns(1) and (2), and now, eqns(20) and (21).

## Conclusions

Recently several research groups<sup>6-10</sup> have used an expression for the rate of the photocatalysed reaction of the form given in eqn(14), where  $\chi_1(-1 + (1 + \chi_2\rho)^{1/2})$  is a replacement for the ' $\alpha\rho^0$ ' term used in the popular rate expressions describing Langmuir and Disrupted Langmuir adsorption kinetics, i.e. eqns (1) and (2), respectively. This replacement provides an explicit function that appears to describe well the observed dependence of reaction rate upon irradiance,  $\rho$ . Unlike other rate expressions, based on quadratic 'P' type models, this explicit function does not contain a quadratic dependence upon  $[P]^{-1}$ . A mechanistic rationale for a quadratic

dependence of rate upon  $\rho$ , but not  $[P]^{-1}$ , is reported here, based on an proposed additional, irreversible hole or  $\text{OH}\bullet$  trapping step. This step carries with it the implication that that the photocatalytic processes involved would usually be expected to have a low quantum yield/quantum efficiency as appears to be the case in the examples cited<sup>6-10,15</sup>. For example, in the photocatalysed oxidation of NO, sensitised by a P25  $\text{TiO}_2$  film<sup>6</sup>, see figure 2, a typical experiment yields a value for  $d[\text{NO}]/dt = 11.3 \times 10^{-9} \text{ mol m}^2 \text{ s}^{-1}$  for  $\rho = 3.15 \times 10^{-6} \text{ mol m}^2 \text{ s}^{-1}$ , suggesting a quantum efficiency = 0.36%. Emeline et al., in their study of the photocatalysed oxidation of PhOH, see figure 3, report a quantum efficiency = 0.6%<sup>15</sup> and Montoya et al., in the study of the photocatalysed oxidation of FA, observe a maximum rate ca.  $= 3.6 \times 10^{13} \text{ molecules cm}^{-2} \text{ s}^{-1}$  using an irradiance  $= 6.2 \times 10^{15} \text{ photons cm}^2 \text{ s}^{-1}$ , i.e. a quantum efficiency = 0.58%<sup>13</sup>. Finally, elsewhere, Passalia et al.<sup>10</sup>, in their study of the photocatalysed oxidation of formaldehyde in air over a  $\text{TiO}_2$  film, using a Langmuir-type rate expression with the form of eqn (21) to fit their data, report a quantum efficiency of only ca. 1.59%. It seems likely this revised version of the Ollis disrupted adsorption model, i.e. eqn(20) will find increasing use by those working in the field. However, as with all kinetic models<sup>3</sup>, just because it fits the kinetic data does not mean it is the actual mechanism and more work is obviously required in order to establish its veracity.

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